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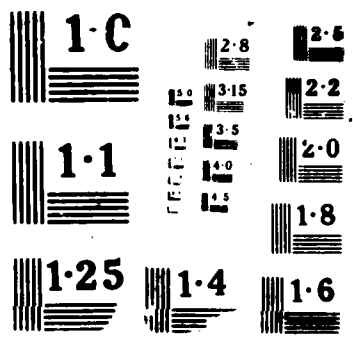
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Electrochromic Cells with Lutetium Diphthalocyanine and  
Semisolid Polymer Electrolytes

by

F. A. Pizzarello and M. M. Nicholson

Science Center  
Rockwell International Corporation  
Anaheim, CA

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**ELECTROCHROMIC CELLS WITH LUTETIUM DIPHTHALOCYANINE  
AND SEMISOLID POLYMER ELECTROLYTES**

F. A. Pizzarello and M. M. Nicholson

**ABSTRACT**

Cyclic voltammograms were obtained for lutetium diphthalocyanine films in contact with plasticized poly(ethylene oxide) (PEO) electrolytes or solvent-swollen 2-acrylamido-2-methylpropanesulfonic acid (AMPS) polymer electrolytes. Cells containing PEO-salt combinations plasticized with propylene glycol (PG) or acetonitrile resulted in slow, nonuniform color changes due to high interfacial resistance. The AMPS cell fabrication was simplified by starting with a commercial AMPS polymer product in the form of a transparent sheet containing water and other additives. This material, when further swollen in a PG-HCl solution, produced the full range of uniform colors, accompanied by well defined voltammograms. It maintained good contact with the dye from -5 to 40°C.

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Thin films of lanthanide diphthalocyanines on transparent conductive electrodes undergo a series of faradaic reactions that result in pronounced color changes. Because of the striking visual effects, fast kinetics, and long-term cycling capability, these electrochromic systems are of major interest for use in flat-panel information displays.<sup>(1,4)</sup> Most investigations of diphthalocyanine electrochromics have been made with aqueous electrolytes. However, many displays users would prefer an all-solid cell. It is also desirable to decrease or eliminate water to avoid film damage resulting from electrolytic gas evolution and to permit operation and storage of the device over a wider temperature range.

In earlier phases of this project, we investigated electrochemical processes occurring within the dye layer during the electrochromic transitions.<sup>(5,6)</sup> More recently, the objective has been to develop solid polymer electrolytes appropriate for use with diphthalocyanine-coated electrodes. Because high transient currents flow during fast color switching, we have sought to enhance the polymer electrolyte conductivity by adding a plasticizer. Technical Report No. 8 under this contract gives results of a conductivity study on several poly(ethylene oxide) (PEO)-salt combinations plasticized with propylene glycol (PG).<sup>(7)</sup> The present report summarizes observations made on lutetium diphthalocyanine electrodes interfaced with plasticized PEO electrolytes and with solvent-swollen semisolid electrolytes containing a polymer of



2-acrylamido-2-methylpropanesulfonic acid (AMPS). Promising results on lutetium diphthalocyanine cells with a different AMPS preparation were reported earlier by Sammells and Pujare.<sup>(3)</sup> The present AMPS electrolytes offer the advantages of easy fabrication and a demonstrated ability to function without loss of electrical contact at temperatures from -5 to 40°C. Further work is needed, however, to make a thorough evaluation of diphthalocyanine-polymer electrolyte cells and develop optimized electrolyte formulations.

## EXPERIMENTAL

The cell structure is indicated in Figure 1. The electrolyte cavity was defined by a polystyrene dam 0.1 cm thick with a circular hole 1.27 cm in diameter, placed directly over the dye film. The counter electrode was an electroformed gold mesh with 80 percent light transmission, which was electroplated with a thin layer of silver. For the AMPS cells, a portion of the silver was anodically converted to AgCl.

PEO films were cast by filling the cavity with an aqueous solution of PEO (MW 4,000,000 from Polysciences) and drying in a stream of nitrogen. A single casting produced a dried-film thickness of approximately  $2 \times 10^{-3}$  cm. The process was repeated when a thicker film was desired. After the polymer was cast, an

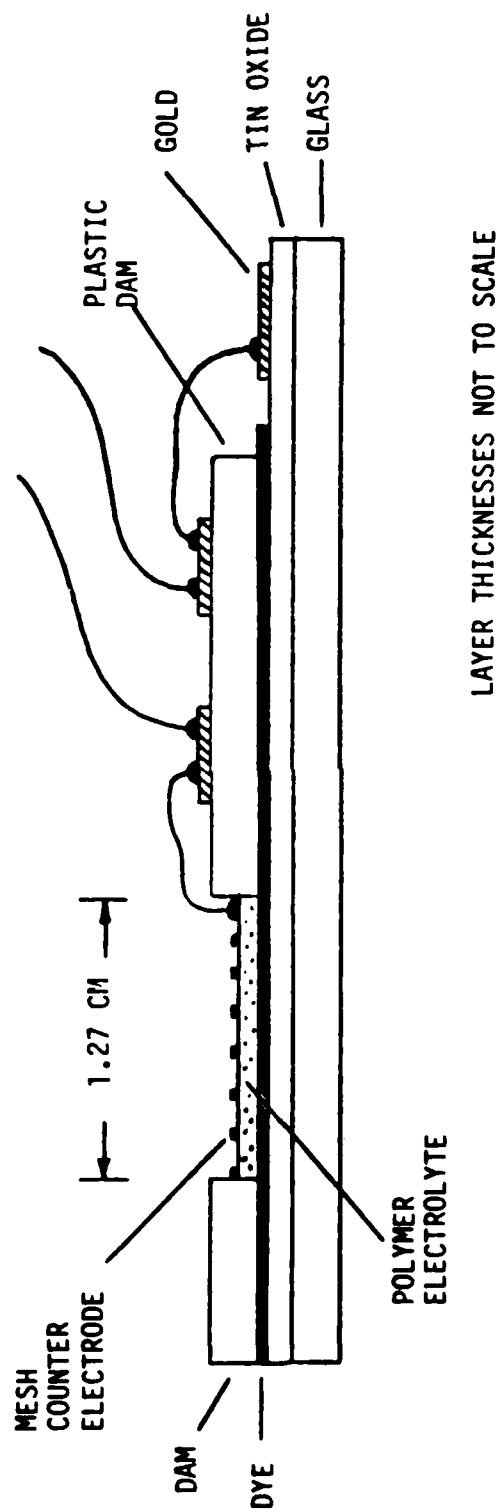


Figure 1. Experimental Cell with Polymer Electrolyte





ionizable component was introduced by contacting the film with a saturated solution of a salt in a selected solvent. The treating solution was LiCl-water, LiCl-PG (1,3-propanediol) or LiCF<sub>3</sub>SO<sub>3</sub>-acetonitrile (AN). Any excess treating solution was removed from the cavity after several minutes and the polymer layer was redried. The mesh counter electrode was then laid on top of the dry electrolyte, and a small amount of PEO solution containing the same salt was added to secure the mesh.

The completed cell was inserted in a controlled-atmosphere chamber constructed from a 1.0 x 4.0 x 8.0-cm Klett colorimeter cell. The lid for this chamber included electrical feedthroughs and gas inlet and outlet tubes. With this arrangement, voltammograms or other current-voltage measurements could be made on the film, and absorption spectra could be recorded in the presence of a controlled atmosphere.

The hardware was the same for the AMPS cells but, instead of solution casting of the electrolyte, a polymer disk of 1.27 cm diameter and approximately 0.15 cm thickness was cut from a preformed sheet of a highly transparent, flexible polyAMPS product. This proprietary material, from Medtronics, Inc., is known as NDO. It contains a polyAMPS salt, water, a humectant, and other additives. The sheet material was used as an expedient to simplify the cell fabrication. The polymer disk was soaked several minutes in a solution of the desired electrolyte and placed on the dye layer. The treating



electrolyte for the AMPS cells was satd aqueous KCl, 1M HCl in water, or 1M HCl in PG prepared by diluting aqueous conc HCl. The final assembly was completed as with the PEO cells.

## RESULTS AND DISCUSSION

Table 1 indicates the components present in the PEO cells and summarizes qualitative observations of the electrode behavior. These electrolytes, containing PEO of MW 4,000,000, proved to be of marginal value, although the cells exposed to acetonitrile vapor were more responsive than those containing only propylene glycol as plasticizer. Murray *et al.* had found AN to be an effective plasticizer of PEO-LiCF<sub>3</sub>SO<sub>3</sub> electrolytes, judged by its effect on voltammograms of redox couples dissolved in the polymer-salt mixture.<sup>(8)</sup> The major problem in our PEO cells appeared to be high resistance at the dye/electrolyte interface. Although the electrolyte conductivity was not measured in these experiments, we had found previously that PEO-LiCl-PG mixtures could reach about  $3 \times 10^{-6} \text{ ohm}^{-1} \text{cm}^{-1}$ .<sup>(7)</sup> This would correspond to a moderate electrolyte resistance of 500 ohms in the cell of Figure 1 if the layer were  $2 \times 10^{-3} \text{ cm}$  thick.

The AMPS type cells were much more responsive, as noted in Table 2. Uniform color changes were obtained and, with HCl present, they covered the full range from violet to orange. These electrolytes contained substantial amounts of water from



TABLE 1  
OBSERVATIONS ON LUTETIUM DIPHthalOCYANINE-POLY(ETHYLENE OXIDE) CELLS

CELL	TREATING SOLUTION	AMBIENT GAS <sup>a</sup>	RESULTS
1	LiCl-H <sub>2</sub> O	Dry N <sub>2</sub> , Followed by N <sub>2</sub> -PG	No color changes. PG increased cell resistance.
2	LiCl-H <sub>2</sub> O	N <sub>2</sub> -PG	Slight change to orange at +2V. No blue color at -3V.
3	LiCl-PG	N <sub>2</sub> -PG	No color change.
4	LiCl-PG	N <sub>2</sub> -PG, followed by N <sub>2</sub> -AN	Slow color change with PG. Orange at +1.5V and blue at -0.5V with AN.
5	LiCF <sub>3</sub> SO <sub>3</sub> -AN	N <sub>2</sub> -AN	Orange and blue Transitions. Faster than Cell 4.
6	LiCF <sub>3</sub> SO <sub>3</sub> -AN	N <sub>2</sub> -AN	Slow, nonuniform color changes.
7	LiCF <sub>3</sub> SO <sub>3</sub> -AN	N <sub>2</sub> -PG	Good color changes initially. Cell then became shorted.

<sup>a</sup>Continuous gas flow.



TABLE 2  
OBSERVATIONS ON LUTETIUM DIPHthalOCYANINE-POLYAMPS CELLS

CELL	ELECTROLYTE TREATMENT		AMBIENT GAS <sup>a</sup>	RESULTS
	SOLUTION	TIME (MIN)		
8	KCl-H <sub>2</sub> O	1	DRY N <sub>2</sub> , FOLLOWED BY N <sub>2</sub> -PG	UNIFORM COLOR CHANGES.
9	1M HCl-H <sub>2</sub> O	5	N <sub>2</sub> -PG	FULL COLOR RANGE ON VOLTAGE SCAN. RAPID RESPONSE INITIALLY; SLOWER ON CONTINUED PG EXPOSURE.
10	1M HCl-PG	5	N <sub>2</sub> -PG	FULL COLOR RANGE; WELL DEFINED VOLTAMMOGRAM; SLOWER ON CONTINUED PG EXPOSURE.
11	PG Only	5	N <sub>2</sub> -PG	FULL COLOR RANGE BUT MUCH SLOWER THAN CELL 10.
12	1M HCl-PG	5	CELL SEALED WITH EXCESS 1M HCl-PG (LIQUID NOT CONTACTING FILM).	FULL COLOR RANGE; WELL DEFINED VOLTAMMOGRAMS. MEASUREMENTS FROM -5 TO 40°C.

<sup>a</sup>Continuous gas flow except in Cell 12.



the AMPS sheet material and the concentrated HCl used to make the acidic glycol solutions. For example, the volatile matter lost on heating the electrolyte in Cell 10 to 200°C amounted to 59% of the total electrolyte weight. Mass spectroscopy showed that the material lost was 36% PG and 64% water by weight. The analysis did not detect HCl. This composition favors low-temperature stability of the electrolyte; in the absence of other components, a 36% PG solution in water freezes at -18°C. It should be possible to increase the proportion of glycol relative to water in the cell by predrying the AMPS sheet before exposing it to the liquid glycol electrolyte.

The better performance of AMPS-HCl-PG cells is reflected in the voltammograms of Figure 2, which cover the temperature range of -5 to 40°C. A comparable voltammogram for AMPS-HCl-H<sub>2</sub>O near 23°C is shown in Figure 3. Intermediate colors due to mixed oxidation states were observed, in addition to those noted on the curve. The PG diminished the rates of the electrochromic reactions, as did the lowering of the cell temperature. The color changes were distinct, at least down to 8°C. For the violet/blue transition, some peak broadening actually could indicate a beneficial effect on device performance; excessively sharp peaks in that region are thought to result from a surface phase transition,<sup>(9)</sup> which would tend to shorten the cycle life.

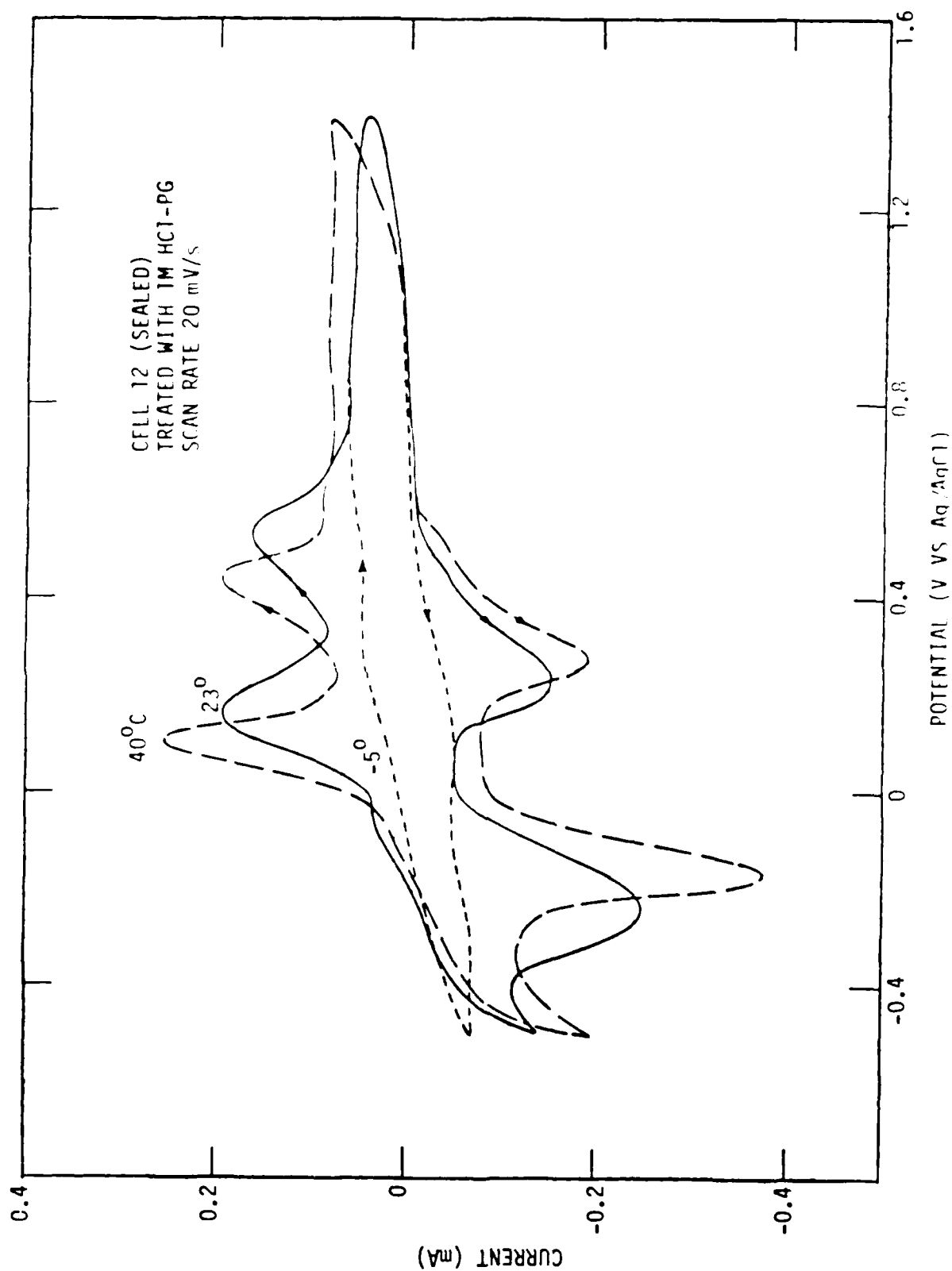


Figure 2. Cyclic Voltammograms for LuPc<sub>2</sub> Cell with Semisolid AMPS-HCl-PG Electrolyte at Different Temperatures

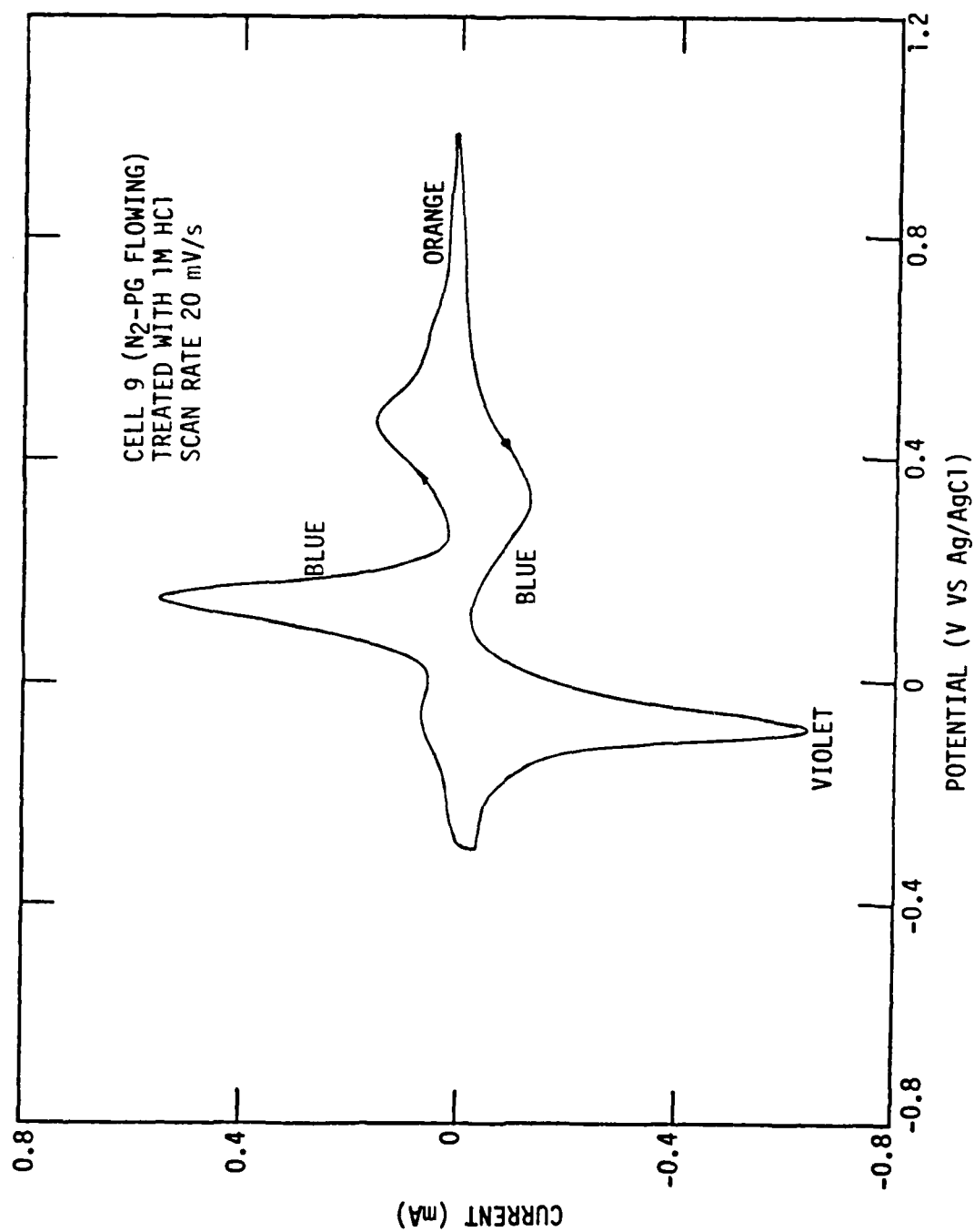


Figure 3. Cyclic Voltammogram for LuPc<sub>2</sub> Cell with Semisolid AMPS-HCl-H<sub>2</sub>O Electrolyte at 23°C



One other observation on the AMPS-PG cells is noteworthy. We found in previous voltammetric experiments that a blue reduced form of lutetium diphthalocyanine dissolved in liquid glycol electrolytes such as KCl-PG. This probably was the limiting factor encountered by Collins and Schiffman in a cycle-life study of this dye in ethylene glycol electrolytes, where the measurements had to be restricted to the orange/green transition.<sup>(4)</sup> In the present study, the reduced dye films showed no tendency to dissolve in the semisolid AMPS electrolytes containing both water and propylene glycol.

#### ACKNOWLEDGMENTS

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